

10/516979



PCT/GB/2003/2501



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REC'D 17 JUL 2003	
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## PRIORITY DOCUMENT

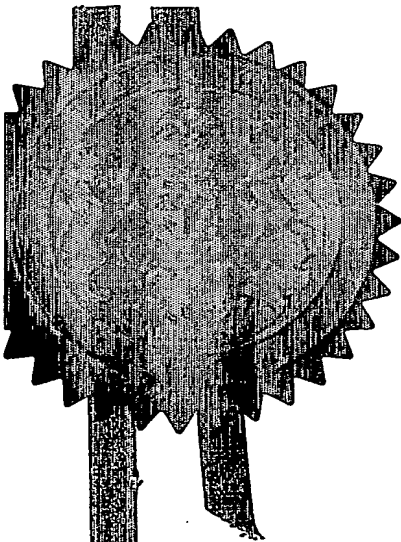
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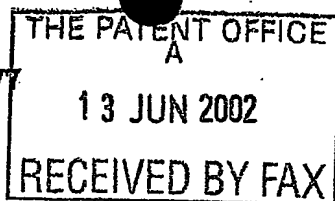


Signed *Andrew Gervay*  
Dated 20 June 2003

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An Executive Agency of the Department of Trade and Industry

Patents Form 1/77

Patents Act 1977  
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13 JUN 2002

**Request for grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
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1. Your reference

P202470

13JUN02 E725320-1 002835

P01/7700 0.00-0213480.7

2. Patent application number

(The Patent Office will fill in this part)

0213480.7

13 JUN 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

A H MARKS AND COMPANY LIMITED  
WYKE  
BRADFORD  
BD12 9EJ

Patents ADP number (if you know it)

838326001

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

POLYMERISATION INHIBITOR

5. Name of your agent (if you have one)

URQUHART-DYKES &amp; LORD

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

TOWER HOUSE, MERRION WAY, LEEDS LS2 8PA

Patents ADP number (if you know it)

1644023

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if

YES

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d))

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**Patents Form 1/77**

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Continuation sheets of this form

Description

6

Claim(s)

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents  
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

13-6-02

12. Name and daytime telephone number of person to contact in the United Kingdom

ROBIN F BROWNE  
0113 245 2388**Warning**

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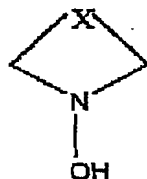
## POLYMERISATION INHIBITOR

This invention relates to compositions for inhibiting polymerisation of unsaturated monomers, particularly vinyl, alphaolefin, acrylic, conjugated diene or other ethylenically unsaturated monomers, and most particularly vinyl aromatic compounds, especially styrene. This invention also relates to a method of inhibiting polymerisation of such monomers.

US 2965685 discloses use of N, N-dialkylhydroxylamines to prevent polymerisation of styrene. Various combinations of N, N-dialkylhydroxylamines with other inhibitors have been disclosed.

According to a first aspect of the present invention there is provided a polymerisation inhibitor comprising a non-hindered cyclic hydroxylamine either alone or in combination with an additional inhibitor.

The non-hindered cyclic hydroxylamine is a cyclic hydroxylamine having no alkyl or other alpha substituents adjacent the hydroxylamine group. Preferred compounds have the formula (1).



(1)

wherein X is a group selected from:  $(CH_2)_m Y (CH_2)_n$  wherein m and n are each independently an integer from 0 to 5 and Y is a  $CH_2$ , or a hetero atom eg O, S or NH and wherein one or more  $CH_2$  is optionally substituted with one or more  $C_1$ - $C_3$  alkyl groups;  $-(CH_2)_r-CH=CH-(CH_2)_s-$  wherein r and s are independently integers from 0 to 3, optionally substituted with one or more  $C_1$ - $C_3$  alkyl groups;

Preferred examples include: 1-hydroxypiperidine, 4-hydroxymorpholine, 1-hydroxypyrrolidine, 1-hydroxyazetidine, 1-hydroxy-2,5-dihydropyrrole, 1-hydroxyhexamethyleneimine, 1-hydroxyazocan. Partially saturated aromatic bi or tricyclic unhindered hydroxylamines may also be employed, for example, selected from:

1-hydroxy-2,3,4-trihydroquinoline, 9-hydroxycarbozole and 1-hydroxy-2,3-dihydroindole. These compounds may be optionally substituted with one or more C<sub>1</sub>-C<sub>5</sub> alkyl groups.

Mixtures of compounds may be employed.

Particularly preferred compounds are selected from: 1-hydroxypiperidine, 4-hydroxymorpholine and mixtures thereof.

The inhibitor in accordance with the first aspect of this invention may be used in combination with one or more co-inhibitors eg nitrophenols such as 2,4-dinitrophenol (DNP) or substituted nitro phenols such as 2-sec-butyl-4,6-dinitrophenol (DNBP). Alternative co-inhibitors may be selected from t-alkylcatechols, t-alkylhydroquinones, benzoquinones, p-phenylene diamines and other inhibitors known to those skilled in the art.

The amount of co-inhibitor may be in the range up to 96%, preferably 40 to 96% by weight of the total amount of inhibitor.

Percentages and other proportions referred to in the specification are by weight unless indicated otherwise. Percentages and proportions may be selected from ranges referred to in the specification to total 100%.

According to a second aspect of the present invention a polymerisation inhibited composition comprises a monomer and an inhibitor in accordance with the first aspect of this invention.

According to a third aspect of this invention a method of inhibiting polymerisation during production, purification, storage or use of a vinyl, alphaolefin, acrylic, conjugated diene or other ethylenically unsaturated monomer comprises the step of addition to the monomer of a polymerisation inhibitor in accordance with the first aspect of the present invention.

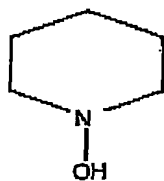
Unhindered cyclic hydroxylamines in accordance with the present invention have been found to be excellent polymerisation inhibitors, particularly of vinyl aromatic compounds,

especially at elevated temperatures. 1-hydroxypiperidine and 4-hydroxymorpholine have been found to be particularly effective inhibitors of styrene polymer formation, both on their own and in combination with 2-*sec*-butyl-4,6-dinitrophenol (DNBP). Unfavourable premature polymerisation in processing steps such as the production, purification, storage, shipment preparation and use of these monomers or in a mixture of the monomers or a hydrocarbon mixture containing such monomers. Premature polymerisation can cause contamination of the monomer and degradation of the properties of the monomer. A polymer can be deposited in the apparatus. Formation of popcorn polymer is particularly undesirable. The polymerisation inhibitor in accordance with the first aspect of the present invention is effective not only for monomers and mixtures thereof but also for hydrocarbon mixtures and the like containing a small proportion of the monomers.

The invention is further described by means of examples but not in any limitative sense.

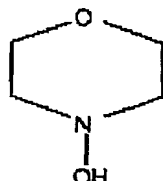
Unhindered cyclic hydroxylamines are disclosed in US 2843481 (Polaroid) and may be prepared by oxidation of the corresponding amines with aqueous hydrogen peroxide at less than 20°C.

#### Structures:



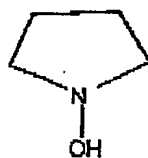
1-H P

M w = 101



4-H M

M w = 103



1-hydroxy-  
pyrrolidine

M w = 87

#### Results

##### (a) Efficacy

Evaluation of the efficacy of hydroxylamines was carried out using a continuous stirred tank reactor (CSTR). These mimic the reboiler of a styrene distillation column. The styrene has a residence time of approximately two hours inside the reactor.

Two CSTRs were used to gather this data. For any given temperature the same CSTR was used for all experiments at that temperature.

120°C CSTR – dead volume was 170 ml. With a styrene flow rate of 75ml/hr the steady state was reached in 4.5 hrs (2 flask volumes). Data gathered after this temperature was averaged to give the steady state polymer level.

110° and 100°C CSTR – dead volume was 150 ml. With a styrene flow rate of 75 ml/hr the steady state was reached in 4 hrs. Data gathered after this point were averaged to give the steady state polymer level.

Nitrogen sparging to remove oxygen was at a measured rate of 200 ml/minute in all experiments. Aside from the inhibitors under test the only variable was the inherent variation in the rate of thermal initiation of styrene polymerisation.

Hydroxylamines were tested on their own and in combination with DNBP as shown in Table 1 (below). By way of comparison results are also presented for prior art styrene inhibitor mixtures, namely 4-Hydroxy tempo with DNBP, 4-Oxo tempo with DNBP and dihydroxypropylhydroxylamine (DHPHA) with DNBP. At a test temperature of 120°C the results shown in Table 1 were obtained (polymer results to nearest 50 ppm). Results within 10% of each other have been ranked as equal.

Table 1 – Results at 120°C Total inhibitor is 400 ppm

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)	Rank
1-HP	100			1850	1
DNBP	90	1-HP	10	2500	2=
DNBP	90	4-HM (100%)	10	2600	2=
DNBP	95.5	4-Oxo Tempo	4.5	2350	2=
DNBP	90	4-Hydroxy Tempo	10	3200	5=
DNBP	100			3350	5=
DNBP	90	DHPHA	10	3450	5=
4-HM (100%)	100			Failed in 3.5 hours	9

Batch tests were also carried out. This was to determine the optimum ratio of DNBP and 4-HM. This was found to be about 7 parts DNBP to about 3 parts 4-HM.

A further continuous test was carried out using this ratio;

Table 1a

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)
DNBP	70	4-HM (100%)	30	1200

At 110°C the results shown in Table 2 were obtained. 4-HM technical grade (65%) showed excellent performance as a single inhibitor at this temperature and therefore the 100% active ingredient was not tested.

Table 2 – Results at 110°C Total inhibitor is 250 ppm

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)	Rank
1-HP	100			100	1
DNBP	90	4-HM (100%)	10	250	2
4-HM (65%)	100			700	3=
DNBP	90	1-HP	10	1100	5
DNBP	90	4-Hydroxy Tempo	10	1600	6
DNBP	90	DHPHA	10	1900	7
DNBP	95.5	4-Oxo Tempo	4.5	2400	9=
DNBP	100			2400	9=

At 100°C the results shown in Table 3 were obtained. As before, the results were given to the nearest 50 ppm of polymer and results within 10% of each other were classed as equivalent.



Table 3 - Results at 100°C Total 100 ppm inhibitor

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)	Rank
1-HP	100			250	1
DNBP	90	4-HM (100%)	10	450	2
DNBP	90	4-Hydroxy Tempo	10	750	3
4-HM (65%)	100			1000	4
DNBP	90	StyrexDHPHA	10	1900	56
DNBP	95.5	4-Oxo tempo	4.5	2150	67=
DNBP	90	1-HP	10	2300	67=
DNBP	100			2750	89

**4-Hydroxymorpholine in 3 component systems**

In this test N-bis-(1,4-dimethylpentyl)-p-phenylenediamine (PD) was used as a third component. The results are shown in Table 4.

Table 4 - Three component mixtures

Test Mixture	Polymer formed at 120°C (ppm)	Polymer formed at 100°C (ppm)
DNB / PD /DHPHA	2750	250
DNBP / PD / 4-HM	1350	100

4-Hydroxymorpholine is clearly a superior enhancer of the DNBP / PD system than is DHPHA under our test conditions. It was noted that at 120°C this three component system is equivalent in performance to the two component DNBP / 4-HM system.

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